Synthesis of perfectly alternating carbon monoxide/olefin polyketones using a sulfonated diphosphine catalyst system

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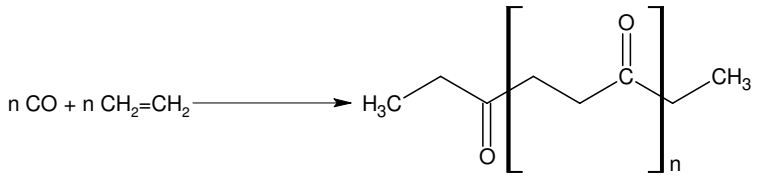
I. Introduction

Abstract

This chapter is an introduction covering the historical development of aliphatic polyketones. Herein the polymerization mechanism and the role played by the catalyst components like the bidentate phosphines ligands and anion, and the polymerization solvent will be described. Finally the scope of this thesis will be presented.

1 Historical development of aliphatic polyketones

The copolymerization of carbon monoxide and an olefin was first achieved in 1941 by Farbenfabriken Bayer[1]. The polymer was produced by the free-radical copolymerization of ethylene and carbon monoxide and the polymer was characterized as a random (non-alternating) polyketone. The reaction conditions were extreme, i.e., 400 bar and 250 °C. In 1950 DuPont[2] showed the possibility of carbon monoxide ethylene copolymerization using free-radical initiation. Their reaction conditions were 500-1500 bar and 25-350 °C. The first perfectly alternating polyketone was synthesized at the Badische Anilin und Soda-Fabrik Aktiengesellschaft in 1951[3] (Scheme 1.1). In this synthesis a $K_2Ni(CN)_4$ catalyst, in water as the solvent, was used to produce perfectly alternating ethylene and carbon monoxide oligomers with a low-melting-point. Next to polymeric products diethyl ketone and propionic acid were formed. The reaction conditions were 100-450 bar and 100-250 °C. Since then continuous improvements have been made in the synthetic procedures, to improve the selectivity, the productivity, and the properties of alternating polyketones by companies such as Shell, BP, BASF, EniChem and academic research groups.



Scheme 1.1. Perfectly alternating ethylene carbon monoxide polyketone.

The work of Sen et al. in 1982 at the Pennsylvania State University[4] and Drent in 1984 at the Shell Company[5] gave new impulses to alternating polyketone synthesis. Sen published the use of dicationic palladium(II) complexes bearing monodentate tertiary phosphines, together with weakly coordinating nitrile ligands and noncoordinating tetrafluoroborate counter ions. The application of this catalyst system enabled the synthesis of ethylene and carbon monoxide copolymers at mild reaction conditions (20-60 bar and 25-60 °C). Drent reported the use of palladium(II)-bidentate phosphine complexes containing weakly coordinating anions for the efficient copolymerization of ethylene and carbon monoxide. The high copolymerization rates (6 kg copolymer (g Pd)$^{-1}$ hr^{-1}) achieved under mild reaction conditions (50-60 bar and 70-135 °C) made ethylene carbon monoxide copolymerization commercially feasible. The discovery of the combination of bidentate ligands and weakly coordinating anions bound to a cationic palladium(II) center has given access to the efficient synthesis of several types of polyketones. This discovery has also resulted in the design of numerous new catalyst systems[6-8] for alternating polyketone synthesis over the last two decades.

Shell Chemicals constructed the world's first commercial alternating polyketone plant in 1996 at Carrington[9] (United Kingdom) with a nameplate capacity of 7000 ton/yr. In this plant the alternating ethylene and carbon monoxide copolymer (Carilon™) was produced. Ketonex™, the BP (British Petroleum) version

of the alternating ethylene and carbon monoxide copolymer, was produced at pilot plant scale in Grangemouth (United Kingdom)[8]. Both companies abandoned their market development efforts on polyketone in 2000/2001.

This chapter summarizes the current state of art of alternating polyketone synthesis. Available literature on catalyst systems, reaction mechanisms, applied reaction solvents and monomer types will be reviewed.

2 Alternating copolymerization of ethylene and carbon monoxide

Several studies have been published on the copolymerization olefins and carbon monoxide but the alternating copolymer of ethylene and carbon monoxide (PK-E) is by far the most studied polyketone composition. The reasons for this focus on PK-E are:

- the base materials are readily available[10]
- the relatively low-cost of the monomers[11]
- the product PK-E (poly-3-oxotrimethylene) is known to have interesting engineering plastic properties, typical for polymers with a high density of heteroatom functionalities[10]
- PK-E has unique chemical and physical properties[6], e.g. mechanical properties, photodegradability, biodegradability and chemical resistance
- new materials can be derived from PK-E by functionalizing the carbonyl groups[12]

The most common catalyst system used for the copolymerization is a cationic palladium complex $Pd(L_2)X_2$ where L_2 represents a bidentate ligand, and X_2 represents a weakly or noncoordinating anion. Structure variation of the bidentate ligand results in significant changes in both the reaction rate and the molecular weight of the product. Also several other types of chelating ligands (e.g. bipyridines, dithioethers and bisoxazolines) can be used.

The counter anions also affect the reaction rate; the highest yields are obtained with very weakly or noncoordinating anions (OTs^-, OTf^-, TFA^-, BF_4^- and ClO_4^-) and with tetra-arylborate anions.

Finally, polyketone catalysis can be carried out in a wide variety of solvents, including water (using sulfonated ligands[13] or by means of emulsion polymerization[14-16]), aprotic solvents (in which aluminoxanes can be used as cocatalysts)[17], ionic liquids[18] (for styrene carbon monoxide copolymerization), supercritical CO_2[19] (using a nickel catalyst) and in solvent-free systems[20]. The most commonly used solvent is methanol.

2.1 Mechanism of polymerization

The reaction mechanism for the alternating copolymerization of ethylene and carbon monoxide using cationic palladium complexes $Pd(L_2)X_2$ involves three important steps: initiation, propagation and termination. These steps will be described in more detail in the next sections.

2.1.1 Initiation

End-group analysis of PK-E products has demonstrated the presence of ester (-$COOCH_3$) and ketone (-$COCH_2CH_3$) functions. It is difficult to determine which group is the “head” and which is the “tail” of the polymer. Beside this combination of an ester and a ketone function, analysis also has shown the presence of diester and diketone compounds[10;21] (Figure 1.1).

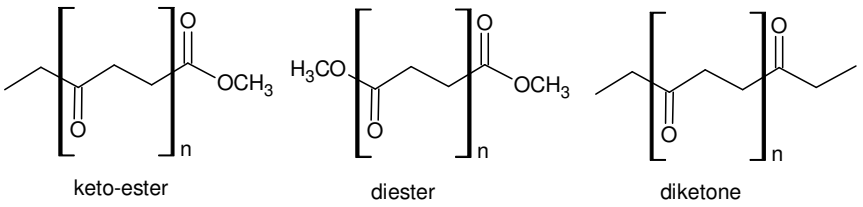
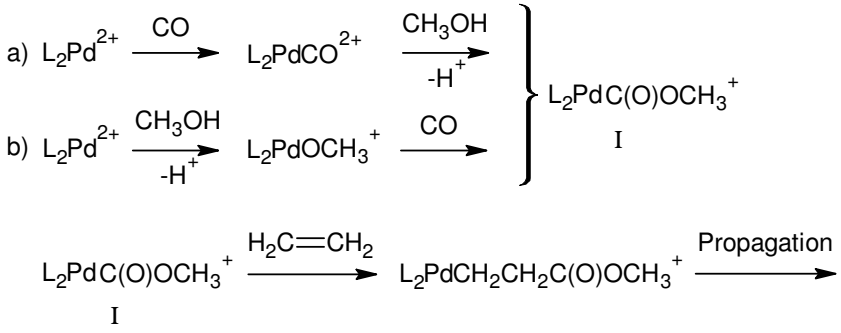


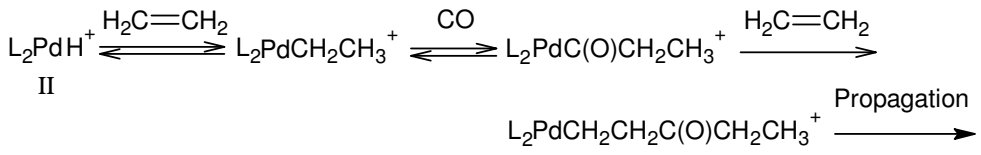
Figure 1.1. PK-E polymer end-groups.

These observations led researchers to propose two initiation and two termination mechanisms for the polyketone formation[10;21]. The first initiation pathway produces ester end-groups. It starts with a palladium carbomethoxy species[10;21;22] (**I**), which can be formed either by direct attack of methanol on coordinated CO (a) or by CO insertion in a palladium methoxide bond (b) (Scheme 1.2).



Scheme 1.2. Ester end-group initiation pathways.

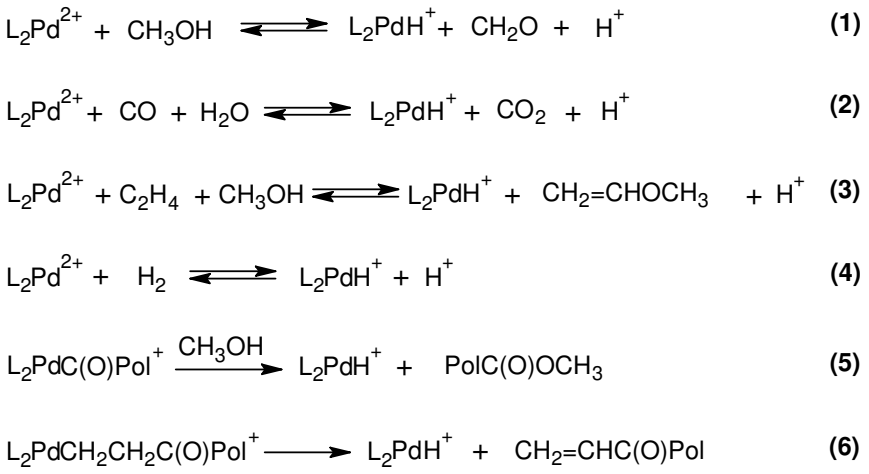
The second initiation pathway starts with the insertion of ethylene in a palladium hydride (**II**) producing a ketone end-group[10;21] (Scheme 1.3). Ethylene insertion in a palladium hydride and CO insertion in the resulting ethyl complex are both rapid and reversible; it is thought that the second ethylene insertion (in the Pd-acyl) is irreversible[10] and starts the chain growth.



Scheme 1.3. Ketone end-group initiation pathway.

These palladium hydride initiators can be generated in six different ways[10]. The first four are a direct result of the start of the catalytic cycle; the latter two are produced by termination steps (Scheme 1.4):

1. By β-hydrogen elimination from palladium methoxide, with the formation of formaldehyde.
2. Via water gas shift reaction forming carbon dioxide.
3. By a Wacker-type oxidation of ethylene forming methoxyethylene.
4. By hydrogen activation (only if present in the reaction medium).
5. By alcoholysis.
6. By β-hydrogen elimination from a growing polymer chain (generally observed with higher olefins and not with ethylene).



Scheme 1.4. Generation of palladium hydride initiators.

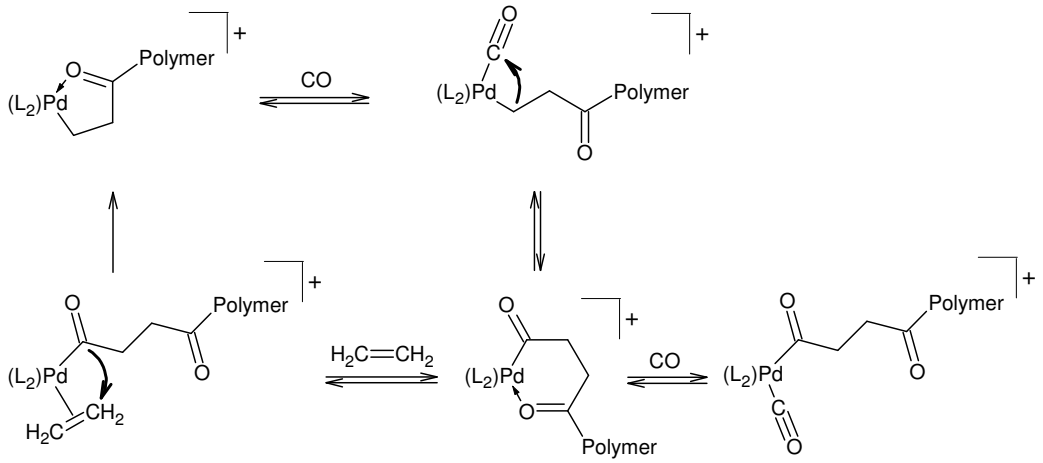
2.1.2 Propagation

The catalytically active species in polyketone formation is thought to be a d^8-square planar cationic palladium complex, i.e., L_2PdPol^+, where L_2 represents the bidentate ligand and Pol the growing polymer chain. An anion, a solvent molecule, a carbonyl group of the chain, or a monomer molecule may fill the fourth coordination site on the palladium center. The competition for the vacant site appears to be an important factor affecting catalysis, and this explains the sensitivity of the system to the choice of solvent and counter-anion. The two alternating propagation steps in the synthesis of PK-E are:

- the migratory insertion of CO into the palladium-alkyl bond and
- migratory insertion of ethylene into the resulting palladium-acyl bond[8;10] (Scheme 1.5).

Carbon monoxide insertion in a palladium-carbon bond is a fairly common reaction. Under polymerization conditions, CO insertion is thought to be rapid and reversible. Olefin insertion in palladium-carbon bonds is not as common, but

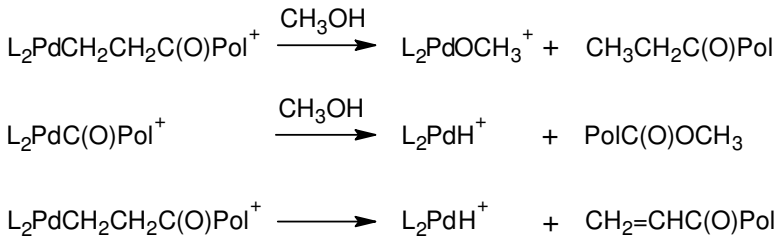
insertions in palladium-acyl bonds appear to be particularly easy. Mechanistic studies of the copolymerization of ethylene and carbon monoxide have shown that the rate of migratory insertion of carbonyl alkyl complexes is much faster than of ethylene carbonyl complexes[23;24]. As a result, it is commonly accepted that olefin insertion is the rate-determining step in polyketone formation.



Scheme 1.5. Proposed propagation mechanism for PK-E[8].

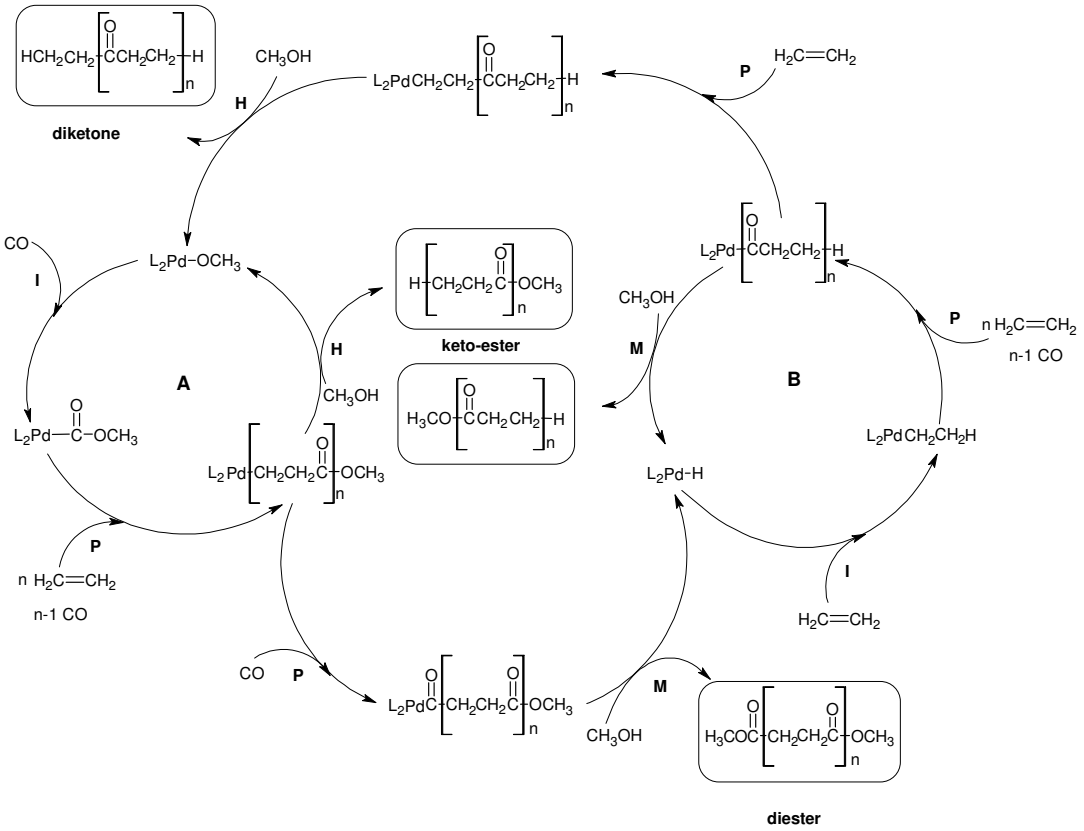
2.1.3 Termination

For ethylene carbon monoxide copolymerization, three relevant termination mechanisms have been proposed[10]. One mechanism, protolysis of the palladium-alkyl bond, produces a saturated ketone end-group (Scheme 1.6). A second mechanism, alcoholysis of the palladium-acyl bond, generates an ester end-group (Scheme 1.6). The last termination step is by β-hydrogen elimination from a growing polymer chain. This is generally only observed with higher olefins and not with ethylene. In general the counter-anion (added as an acid) used in the reaction is added in excess, this extra counter-anion and hence extra protons could also participate in the protolysis termination mechanism.



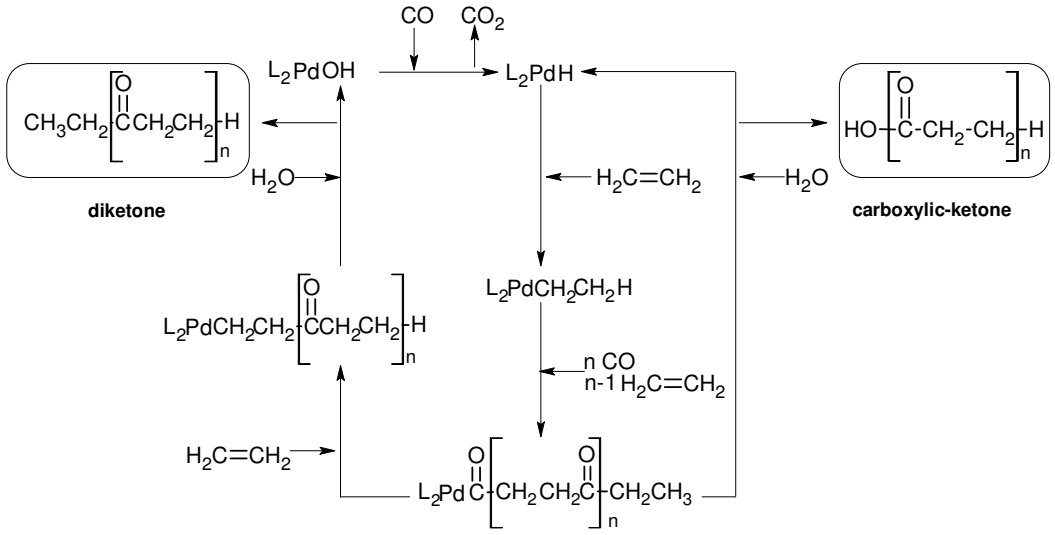
Scheme 1.6. Protolysis (upper), alcoholysis (middle) and β-hydrogen elimination (lower) termination pathways.

Scheme 1.7 summarizes the formation of the three possible polymeric products in the ethylene carbon monoxide copolymerization by the two initiation-propagation-termination cycles **A** and **B**[10]. Both cycles produce keto ester molecules, but the cycles are connected by the two "cross" termination steps that lead to diester and diketone products.



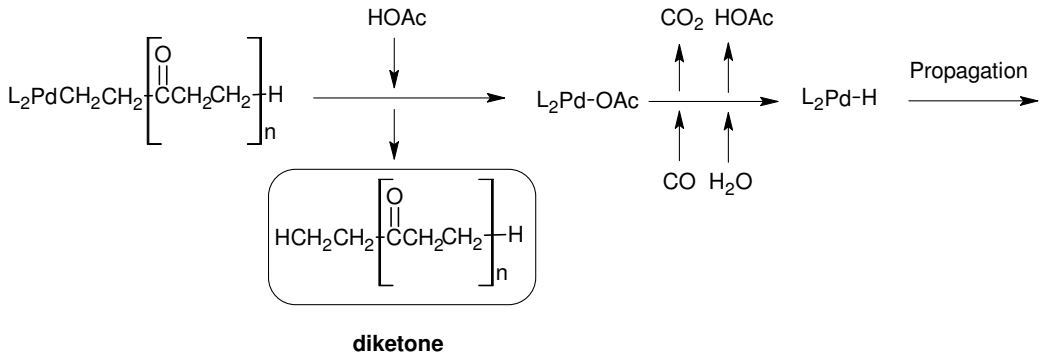
Scheme 1.7. Proposed mechanism of ethylene and carbon monoxide copolymerization by a L_2Pd catalyst, where L_2 represents a diphosphine ligand[10]. (I = initiation, M = methanolysis, H = protolysis and P = propagation)

When water is used as the solvent, the chain growth is terminated by hydrolysis of either a palladium-acyl or a palladium-alkyl bond, resulting in the formation of a carboxylic or a keto end-group, respectively[25;26] (Scheme 1.8).



Scheme 1.8. Proposed mechanism of ethylene and carbon monoxide copolymerization in water by a L_2Pd catalyst, where L_2 represents a diphosphine ligand[25;26].

In case acetic acid is present in the reaction solvent, this can also play a role in the termination step to form ketone end-groups[27]. The acetic acid terminates the chain growth by protonating the palladium-alkyl bond (protonolysis) forming a $[Pd(OAc^-)]^+$, which in turn reacts with water and carbon monoxide forming a palladium hydride initiatior, acetic acid and CO_2 (Scheme 1.9).

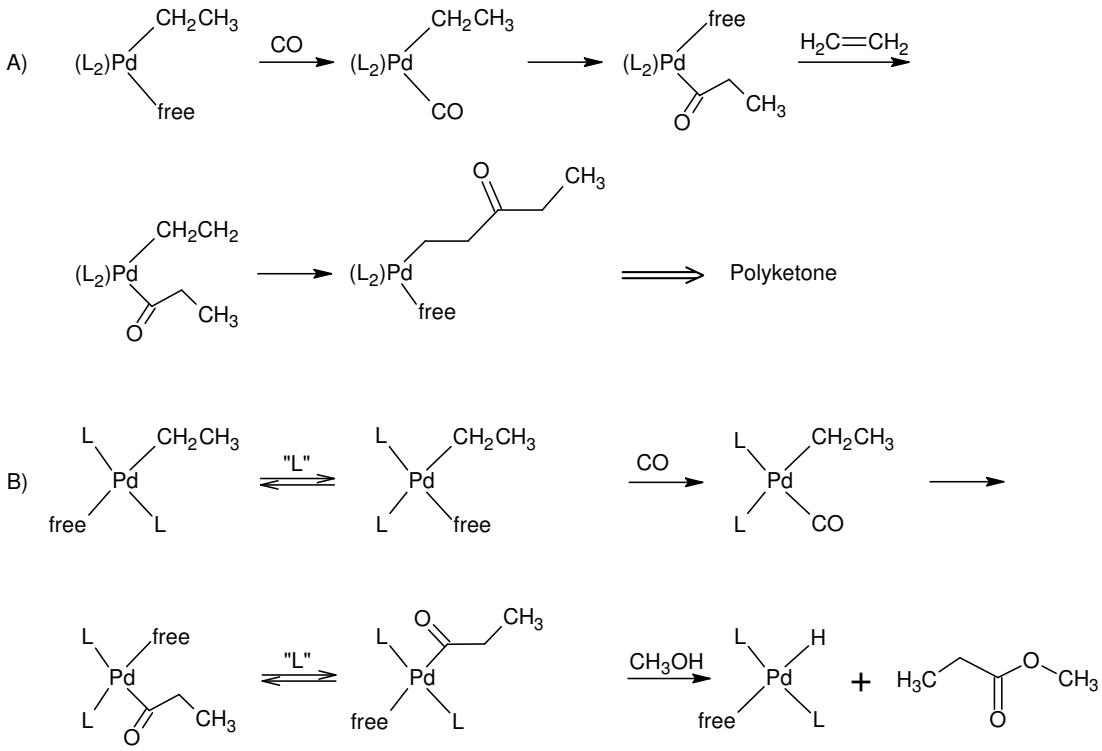


Scheme 1.9. Chain growth termination by acetic acid in the copolymerization of ethylene and carbon monoxide[27].

In summary, when water, methanol and/or acetic acid are present in the solvent mixture, a combination of the mechanisms shown in schemes 1.7, 1.8 and 1.9 can be expected[28].

2.2 The role of bidentate ligands

Under conditions of polyketone catalysis, where a cationic palladium(II) complex $Pd(L_1)X_2$ is used, with L_1 representing a monodentate ligand and X_2 a Brønsted acid of weakly coordinating anions, the monodentate ligand will selectively generate methyl propionate. When using a bidentate ligand polyketone is formed instead of the methyl propionate[10]. The difference in chemo selectivity might be due to the difference in coordination of the ligands on the palladium center. Monodentate ligands can coordinate in both *cis* and *trans* fashion, while bidentate ligands are always *cis* coordinated. The fact that the starting (or growing) polymer chain and the "empty" fourth coordination site are always *cis* to each[10] other makes olefin insertion in the palladium-acyl bond easy when diphosphine complexes are used (Scheme 1.10 A). When monodentate phosphines are used, both Pd-alkyl and Pd-acyl species prefer a *trans* orientation of the phosphine ligands for steric reasons and probably also because it avoids the unfavorable situation of a Pd-P bond *trans* to a Pd-C bond. At the same time when the phosphine ligands (L) are present in excess *cis/trans* isomerization is expected to be rapid. It is assumed that both the insertion of ethylene in Pd-H and the insertion of CO in Pd-alkyl can occur only when the phosphine ligands are oriented in *cis* fashion. Immediately after insertion, a *cis/trans* isomerization (caused by the excess ligand) is likely to occur which places the "chain" and the fourth site *trans,* which is unfavorable for further monomer insertions and so the Pd-acyl will terminate giving methyl propionate[10] (Scheme 1.10 B).



Scheme 1.10. The effect of bidentate and monodentate ligands in the chemo selectivity of the reaction giving respectively polyketone (A) and methylpropionate (B).

2.2.1 Diphosphine ligands

Diphosphine ligands are the most common ligands used in the copolymerization of ethylene and carbon monoxide. Figure 1.2 shows a selection of some of these ligands[8].

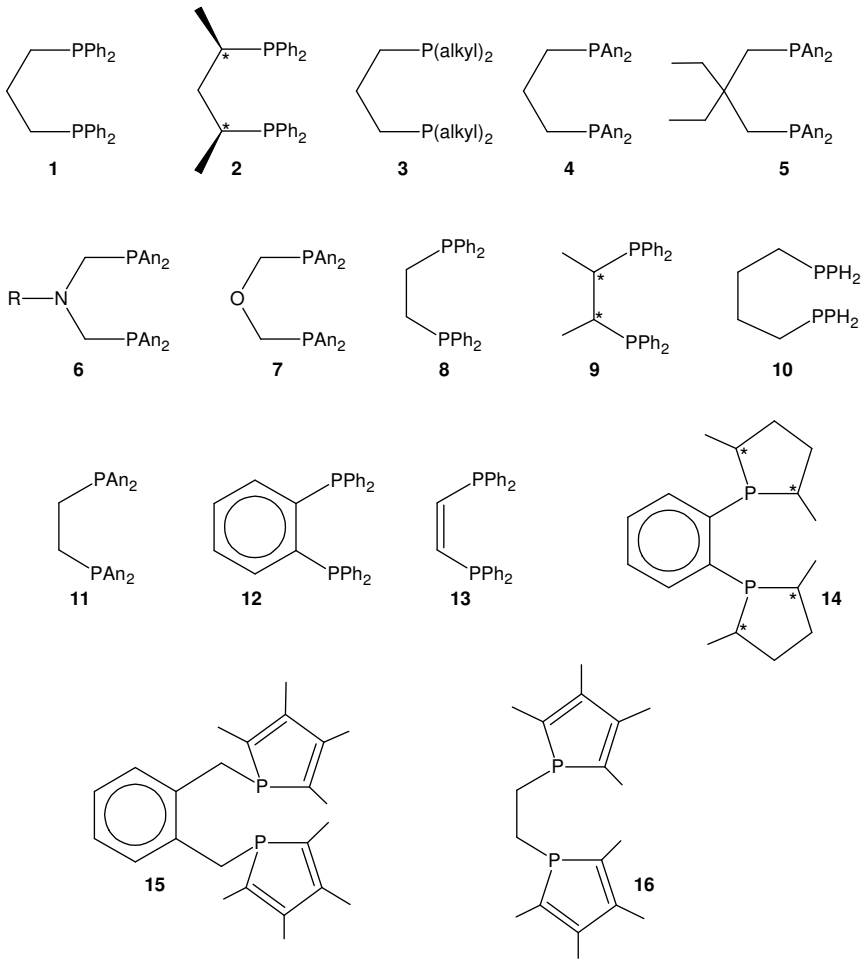
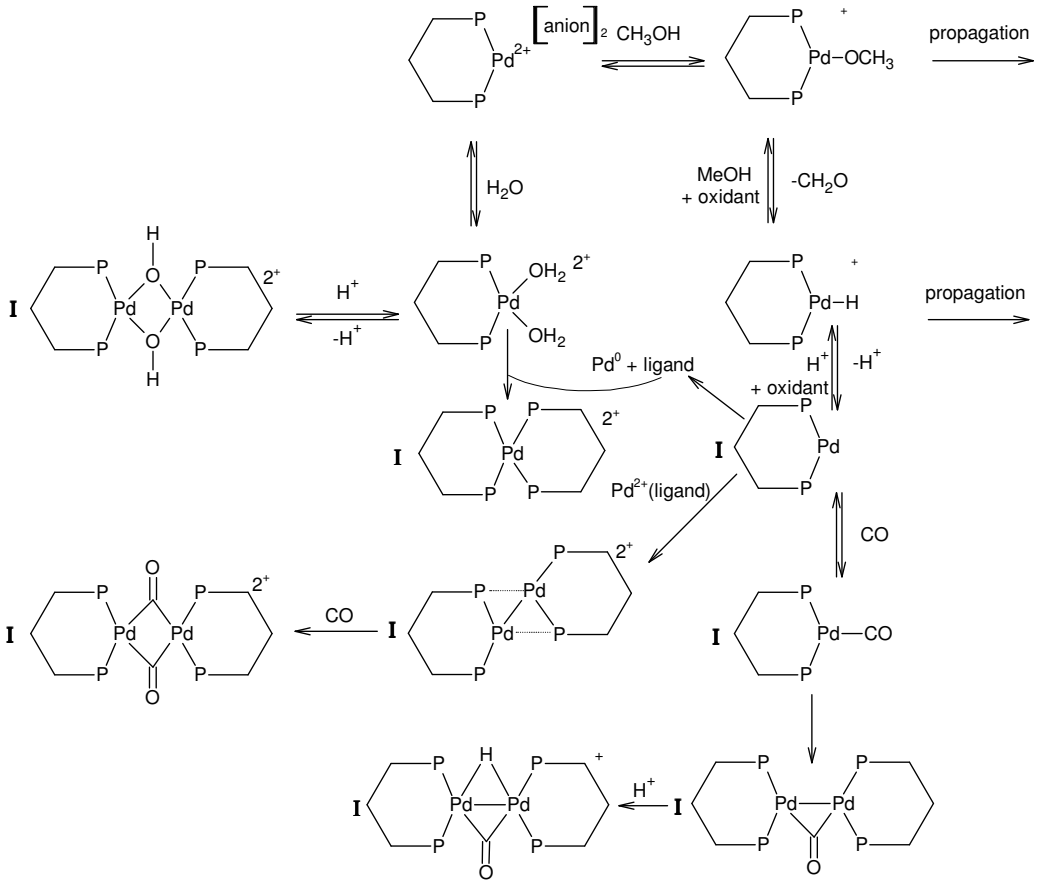


Figure 1.2. Diphosphine ligands used in the copolymerization of olefins and carbon monoxide[8]. An = 2-anisyl (methoxybenzene), R = tBu or Ph.

One of the drawbacks of Pd^{II}-diphosphine catalysts is their facile degradation (formation of inactive Pd^0-species) under polyketone synthesis conditions[6]. For example it is known that $(dppp)PdH^+$ (**I** in Figure 1.2) is not stable in methanol and slowly undergoes deprotonation with formation of $(dppp)Pd^0$ which may either separate into Pd metal and free ligand or couple with $(dppp)Pd^{2+}$ to form the catalytically inactive binuclear complex $[Pd(dppp)]_2^{2+}$ [6]. These deactivation steps are usually in equilibrium. The possible deactivation pathways for $(dppp)Pd^{2+}$ catalyst are shown in (Scheme 1.11). These steps are also expected to happen with other Pd(II)-diphosphine catalyst systems.



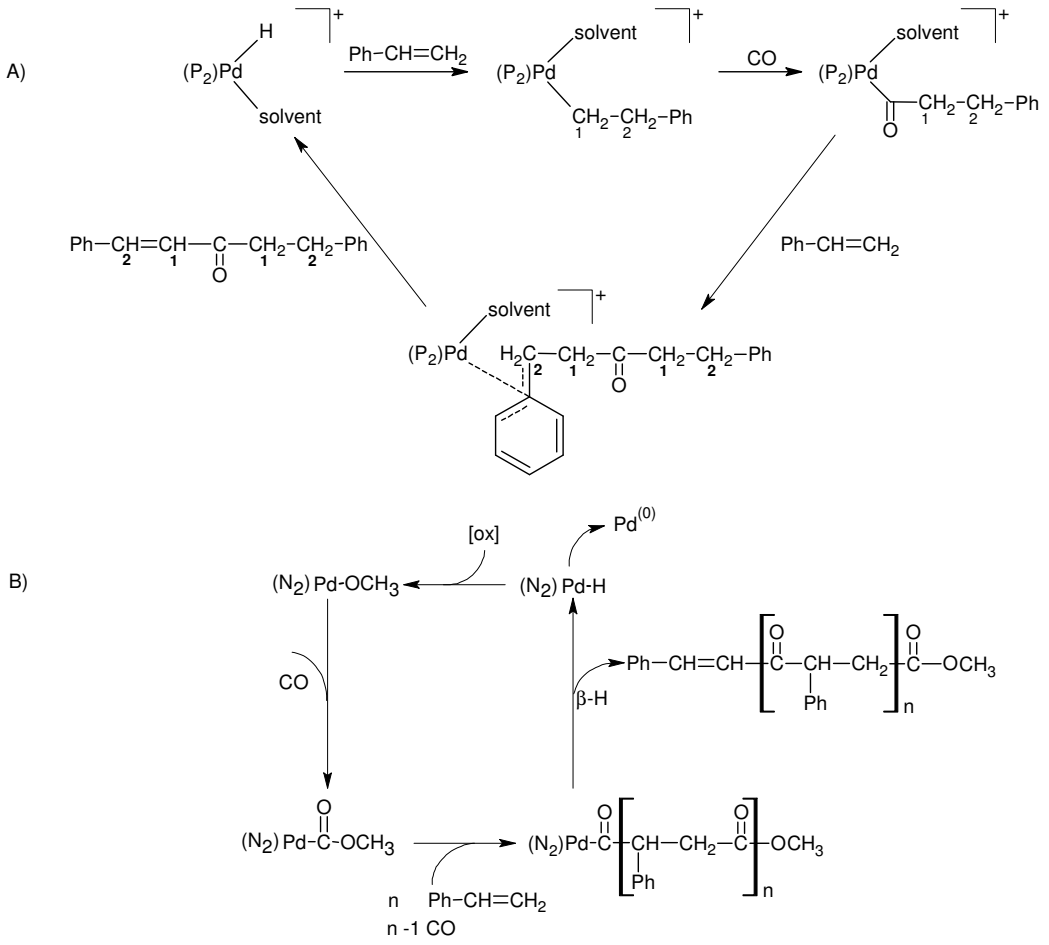
Scheme 1.11. Deactivation pathways of Pd(II)(dppp) catalyst under PK-E polymerization conditions[6]. (Inactive catalyst species shown as I)

2.2.2 Dinitrogen Ligands

The general mechanistic steps for phosphine-modified Pd catalysts also are considered valid for dinitrogen ligands or any other bidentate chelating ligand that is effective as a copolymerization catalyst. Many dinitrogen ligands (e.g. bipy, phen and bis(arylimino)acenaphthene (Ar-BIAN)) form active copolymerization catalysts in conjunction with Pd(II) ions, but the activity is generally lower than with dppp-based catalysts. Dinitrogen ligands have also been widely used in mechanistic studies of olefin carbon monoxide copolymerizations[23]. The insertions of CO into Pd-CH_3 and of strained alkenes into Pd-COR complexed by various dinitrogen ligands have been studied[29]. In analogy to similar reactions involving diphosphine ligands[30;31], it was found that rigid dinitrogen ligands (e.g. Ar-BIAN) have an activating effect on the insertion of both CO and olefins into Pd-C bonds. It is proposed that ligand rigidity disables dissociation of one ligating nitrogen, and hence stabilizes the N-Pd-N metalla-ring[29].

The use of dinitrogen ligands in the synthesis of polyketones has been very important, especially in the copolymerization of aromatic olefins such as styrene and its derivatives. In general diphosphine ligands are preferred for co- and terpolymerizations of aliphatic α-olefins, while for the same reaction with aromatic

olefins bidentate nitrogen or hybrid phosphine-nitrogen ligands are preferred[32]. One example is the copolymerization of styrene and carbon monoxide. With diphosphine ligands such as dppp only unsaturated monoketones are produced (Scheme 1.12A[33]), whereas copolymers are produced with dinitrogen ligands (Scheme 1.12 B[10]).



Scheme 1.12. Styrene carbon monoxide copolymerization with diphosphine (A) and dinitrogen (B) ligands.

The reaction mechanism of CO/styrene copolymerization with diphosphine ligands shows that the reaction is initiated by insertion of styrene in a palladium hydride in the 1,2-insertion mode, followed by CO insertion forming a palladium acyl bond. The second styrene is inserted in the 2,1-insertion mode forming palladium (secondary) hydrocarbyl. Styrene inserts in Pd-acyl exclusively in the 2,1-insertion mode; probably due to steric hindrance between the acyl group and the phenyl group in the 1,2-insertion mode and/or due to interaction between the palladium center and the phenyl ring during insertion which provides a lower energy insertion pathway[10]. This palladium diphosphine (secondary) hydrocarbyl is highly prone to β-hydrogen elimination and hence gives the 1,5-diphenylpentyl-1-

en-3-one monoketones instead of further propagation into polyketones[33]. When dinitrogen ligands are used, the reaction is initialized by a CO insertion into a palladium methoxy species forming a palladium acyl (or carbomethoxy) species. Because of the acyl group the styrene is inserted in the 2,1-insertion mode, at this moment β-hydrogen elimination is highly prone. However this β-elimination tendency is decreased due to the dinitrogen ligand favoring propagation till at a certain point the reaction is terminated by β-hydrogen elimination. During this termination palladium hydrides are formed which have the tendency to decompose to palladium metal. Therefore an oxidant (ox) is added to re-oxidize this back to a palladium methoxide. So palladium hydride is inactive for CO/styrene copolymerization which is contrary to CO/ethylene copolymerization where it forms an important initiator for the copolymerization.

The difference between the diphosphine and dinitrogen ligands lies in the difference of electrophilicity of the palladium center. With diphosphine ligands the palladium center has a higher electron density which is more favorable for β-hydrogen elimination compared to the lower electron density when dinitrogen ligands are used[6;10]. Another probable reason is that the diphosphine palladium styryl intermediates formed in the initial steps of the CO/styrene copolymerization with palladium hydrides are strongly stabilized by π-benzylic or β-aryl coordination (Figure 1.3), which inhibits the CO insertion and leads to decomposition of the intermediates into palladium metal[6;34]. This inhibition occurs at relatively low temperatures (25-75 °C)[10] and could also occur after a second styrene insertion[34], which would then lead to a monoketone product due to fast β-hydrogen elimination.

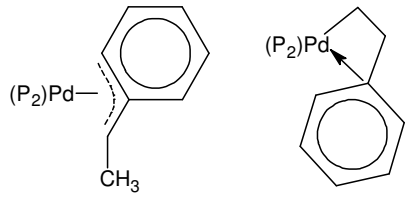


Figure 1.3. Palladium styryl coordination.
π-Benzylic (allylic) coordination after 2,1-insertion (left) and β-aryl coordination after 1,2-insertion (right).

2.2.3 Miscellaneous ligands

Besides diphosphine and dinitrogen ligands, also N-O, N-P, P-S and P-O combinations have been used for the copolymerization of carbon monoxide and olefins. Examples of these ligands in literature are:

Table 1.1. Examples of N-O, N-P, P-S and P-O ligands.

Ligand	Example
N-O[35]	Me-pic, Me-6-Me-pic, N,N-dipPLA and 6-Me-N,N-dipPLA
N-P[36]	PCH_{2OX} and PCH_{2OX}^{Me2}
P-S[37]	diphenyl[2-(phenylsulfinyl)ethyl]phosphine
P-O[38]	dppmO, dppeO, dpppO and dtolpmO

The structures of the ligands are shown in Figure 1.4.

The copolymerization mechanism for these ligands is different from the one reported for diphosphine ligands. The mechanism can be much more complex[35].

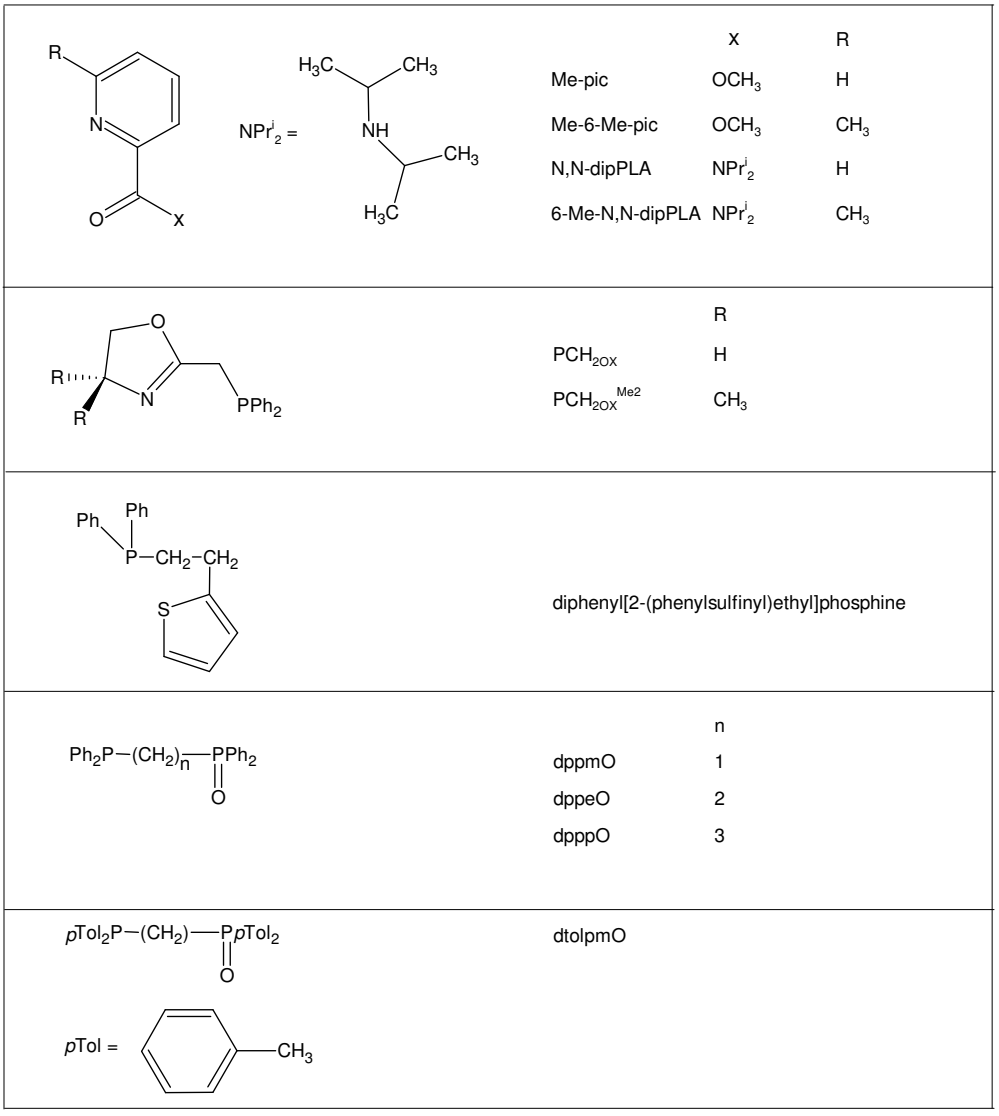


Figure 1.4. Ligands mentioned in Table 1.1.

2.3 The role of the anions

Anions also play an important role in the copolymerization of carbon monoxide and olefins. These anions are required to be weak or noncoordinating. The anions are expected to enable easy access of the monomers to the coordination sites at the metal center. It is also expected that the anions have an effect on the catalytic cycle. Depending on the anion it can form a cation-anion pair with the metal center. The strength of this cation-anion pair generates a more or less electrophilic metal center. A more electrophilic metal center will affect the binding energy of the monomers. This results in a less stable intermediate catalyst

species and a higher rate of monomer insertion into the growing polymer chain. It is important to take into account that this interaction between metal center and anion depends on the properties of the solvent used in the copolymerization reaction as the ease of dissociation of the anion from the cation strongly depends on solvent polarity. Hence it must be understood that it is possible to have an anion, which can show a lower catalyst activity in a certain solvent but be very active in another one. The best results in polar solvents like methanol are obtained with OTs^-, OTf^-, TFA^-, BF_4^-, and ClO_4^- as the anions. It is not always necessary to add an anion to the catalyst system, the anion present in the metal precursor can also affect the electrophilicity of the metal center[39].

2.4 The role of the solvent

Methanol is the most commonly used solvent in olefin carbon monoxide copolymerization. Other solvents used are:

- water[12;18;25;39-41]
- acetic acid[12;39]
- methyl acetate[12]
- hexylpyridinium bis(trifluoromethanesulfonyl)imide[18] (ionic liquid)
- acetonitrile[42]
- tetrahydrofuran[42]
- dichloromethane[32;43]
- chloroform[4]
- trifluoroethanol[44]
- different combinations of these solvents

The choice of a solvent depends on different criteria: the solubility of the monomers in the solvent should be high, the catalyst should be soluble in the solvent, the catalyst should be stable in the solvent, the counter-anion of the catalyst system should be weakly or noncoordinating in the solvent and, of course, the catalyst activity in the solvent should be high.

In this research the following four solvents were used: methanol, water, acetic acid and methyl acetate. The effect of these solvents on polyketone synthesis will be described briefly.

Methanol

1. Monomers like carbon monoxide, ethylene and propylene are more soluble in methanol than in water and acetic acid[28].
2. Diphosphine based catalyst systems exhibit a lower stability in methanol, Section 2.2.1.

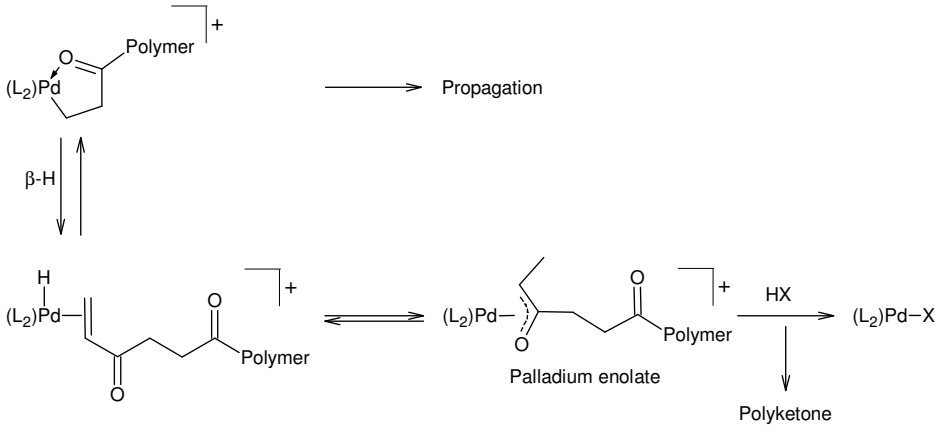
Water

1. In water anions are expected to have a weaker anion to metal coordination than in organic solvents (water has a higher solubility parameter than methanol, respectively δ 47.8 and 29.6 $MPa^{1/2}$ [45]).

2. It is known that water (in appropriate amounts) also has a promoting effect on the catalyst activity, because it favors the formation of palladium hydride (via watergas shift reaction, Section 2.1.3) which is an initiator of the reaction.
3. Water might also inhibit dimerisation of the palladium catalysts. Generally palladium catalyst dimers are less or even inactive species[27].
4. Water coordinates to the palladium(II) cation more strongly than for example methanol, which can result in a reduced accessibility for the incoming monomers[13].
5. Monomers like carbon monoxide, ethylene and propylene have a low solubility in water[28].
6. Water and highly viscous polyketones (i.e., high propylene content polyketones) can form highly viscous slurries, which can lead to mass transfer limitations in the slurry.
7. Water could decrease the molecular weight of the polymers since it is also involved in the termination reaction (Section 2.1.3).

Acetic acid

1. The acetic acid (although a weak acid) could also donate a proton to form palladium hydride (Section 2.1.3).
2. The acetic acid may prevent deprotonation of the active palladium hydride, reducing the degradation rate of the catalyst[6;27].
3. Strong protic acids remove strongly bound monomers from palladium[46]. These acids usually have a pKa ≤ 4. Acetic acid has a pKa of 4.76[47] so, although to a lower extent, it could also have the same effect as that of the strong protic acids.
4. Strong acids can remove ligands from the less active palladium dimer complexes and hence deliver the Pd(II) monomer complex[46] (*vide supra*).
5. The anion of the acetic acid (OAc^-) could also compete with the coordination sites on the catalyst, which inhibits the formation of enolates (intermediate species between propagation and termination, Scheme 1.13), so the polymerization process proceeds further (higher molecular weights), however due to competition of the monomers with the OAc-anion at a lower rate[27].

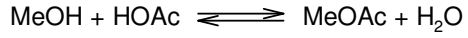


Scheme 1.13. Formation of palladium enolate.

6. The acetic acid seems to also facilitate the opening of the five- or six-membered rings involved in the catalyst cycle[27].
7. Good solubility of monomers compared to water[28].

Methyl acetate

1. In a methanol and acetic acid solvent mixture methyl acetate and water can be formed (Scheme 1.14). To optimize this equilibrium methyl acetate and water are added to the mixture.



Scheme 1.14. Equilibrium solvent mixture.

2. Methyl acetate has a solubility parameter of 18.7 $MPa^{1/2}$ [45], while acetic acid has a solubility parameter of 21,4 $MPa^{1/2}$ [45], this could indicate that the solubility of the monomers are as good in methyl acetate as in acetic acid.

3 Alternating co- and terpolymerization of other olefins and carbon monoxide

Beside ethylene as the monomer, also other olefins can be copolymerized into alternating polyketones. Depending on the type of olefin used, the new polymer will exhibit different physical and chemical properties. Essentially the same catalysts used for ethylene and carbon monoxide copolymerization can be used for other olefins. Examples of olefins used in polyketone synthesis are:

- cyclopentene[42]
- 2-aryl-1-methylenecyclopropanes[42]
- methylenecyclopropane[42]
- vinyl acetate[48]
- propylene (PK-P)[49]
- fluoroalkenes[43]
- styrene[18;32;50;51]
- *tert*-butylstyrene[51]
- dicyclopentadiene[10]
- norbornadiene[4]
- norbornylene[4]
- combinations of different olefins[12;26;52]

4 Scope of this thesis

As already mentioned in the previous sections, alternating polyketones are known to have interesting engineering plastic properties. Applications are expected in the fields of molded parts, foams, coatings, castings, additives and fibers. The fact that the carbonyl groups on the polyketone can be functionalized

into a variety of new materials is also an interesting property. It is expected that from polyketones the following new polymers can be synthesized:

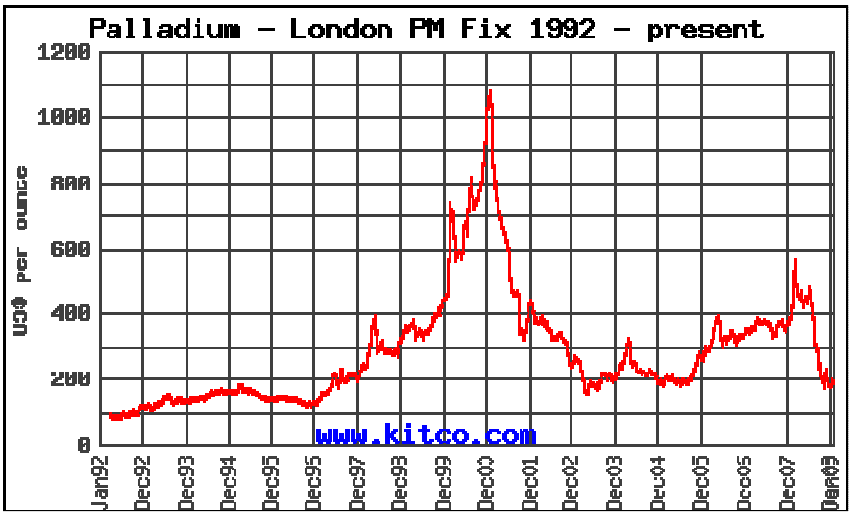
Table 1.2. Expected products from polyketone functionalization.

New Polymers	By reaction with
Polyalcohols[53]	hydrides
Keto-furans[54]	acids
Carboxyl-pyrroles[55-58]	amino-acids
Pyrroles[59]	ammonia
Poly-phenols[60]	phenol
Amino-pyrroles[55;56;58;61;62]	amines

Although it is clear that polyketones offer great potential in different application areas, commercial manufacturing processes no longer exist. Until now the highest catalyst activities were achieved using palladium based diphosphine catalysts. Palladium is not only an expensive noble metal but its price is very unstable as can be seen in Graph 1.1. The palladium price over the last 17 years was:

- Low (1992) : 100 US$ per ounce / 2100 € per kilogram.
- High (2000) : 1100 US$ per ounce / 23500 € per kilogram.
- Intermediate (December 2008): 200 US$ per ounce / 5000 € per kilogram.

Another problem is that the catalyst activities are still relatively low. Both factors are responsible for high polyketone production cost.



Graph 1.1. Palladium price history. Source: www.kitco.com.

Mul W.P. et al.[12] showed that the palladium based catalyst systems $Pd(BDOMPP)(TFA)_2$, $Pd(BDOMPP\text{-}S[Na]_4)(TFA)_2$ and $Pd(BDOMPP\text{-}S[H]_4)(TFA)_2$

are among the most active catalyst systems in the synthesis of ethylene (PK-E) and ethylene/propylene (PK-EP) based polyketones. BDOMPP stands for (1,3-bis(di-(*o*-methoxyphenyl)-phosphino)propane) and BDOMPP-S for 1,3-bis(di-(*o*-methoxy-*m*-sulphonatophenyl)-phosphino)propane. These catalyst systems are not only highly active but the BDOMPP-S based catalyst systems are also recyclable. The combination of a high activity and recyclability makes these catalysts attractive for polyketone production at lower costs.

The objective of this project is the development of an efficient and recyclable catalyst system for the copolymerization of carbon monoxide and olefins. To achieve this objective the BDOMPP and BDOMPP-S$[H]_4$ catalysts used by Mul W.P. et al.[12] will be studied in more detail. The target products in this research are PK-EP polymers with a molecular weight (M_n) of 2000-5000 g/mole and an ethylene content ($C_2^=$, based on total olefin insertion) of 0-50 mol%. These specifications were chosen because knowledge on the synthesis of co-/terpolymers in this range is limited, while their thermoset polymer applications and their modification to new class of functionalized polymers offer great potential for the development of new product concepts in several end-use sectors[61;62].

This thesis presents the results of polymerization studies using different reaction conditions, different catalysts and different monomer compositions.

Chapter 2 describes the results obtained with different solvent compositions for the terpolymerization of ethylene, propylene and carbon monoxide (PK-EP) with the [Pd(BDOMPP-S$[H]_4$)][TFA]$_2$ catalyst system. Herein the effect of solvent on catalyst performance, polymer microstructure and molecular weight will be described.

The synthesis of PK-EP was further studied using the [Pd(BDOMPP-S$[H]_4$)][TFA]$_2$ catalyst system in a methanol/water/acetic acid/methyl acetate solvent mixture under different reaction conditions in Chapter 3.

Chapter 4 presents the results of studies aimed at creating basic understanding concerning the phenomenon that the addition of particular salts to the reaction system enhances the activity of the used catalyst.

In Chapter 5, five different catalyst systems based on BDOMPP-type ligands will be studied in the synthesis of PK-EP.

The catalyst systems applied in the synthesis of PK-EP were also studied in the alternating copolymerization of propylene and carbon monoxide (PK-P). The synthesis of this copolymer in different solvents will be described in Chapter 6.

Nomenclature

Abbreviations

An	2-anisyl (methoxybenzene)
Ar- BIAN	bis(arylimino)acenaphthene
BDOMPP	1,3-bis(di-(*o*-methoxyphenyl)-phosphino)propane
BDOMPP-S$(H)_4$	1,3-bis(di-(*o*-methoxy-*m*-sulphonatophenyl)-phosphino) propane (protonated form)
BDOMPP-S$(Na)_4$	1,3-bis(di-(*o*-methoxy-*m*-sulphonatophenyl)-phosphino) propane (sodium salt form)
BF_4^-	tetrafluoroborate anion
bipy	2,2'-bipyridine
ClO_4^-	perchlorate anion
dppeO	[2-(diphenylphosphino)ethyl]diphenylphosphine oxide
dppmO	(diphenylphosphinomethyl)diphenylphosphine oxide
dpppO	[3-(diphenylphosphino)propyl]diphenylphosphine oxide
dtolpmO	bis(di-*o*-tolylphosphino)methane-monoxide
g	gram
L	ligand
L_2	represents the bidentate ligand
Me-6-Me-pic	methyl 6-methylpicolinate
6-Me-N,N-dipPLA	6-methyl-*N,N*-diisopropylpicolinamide
Me-pic	methylpicolinate
N,N-dipPLA	*N,N*-diisopropylpicolinamide
OTf^-	trifluoromethanesulfonate (triflate) anion
OTs^-	*p*-toluenesulfonate (tosylate) anion
PCH_{2OX}	(2-oxazoline-2-ylmethyl)diphenylphosphine
PCH_{2OX}^{Me2}	(2-oxazoline-2-ylmethyl-4,4-dimethyl)diphenylphosphine
Pd	palladium
phen	phenantroline
PK	polyketone
PK-E	ethylene based polyketone
PK-EP	ethylene-propylene based polyketone
PK-P	propylene based polyketone
Pol	growing polymer chain
TFA^-	trifluoroacetate anion

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